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Polyhedron 22 (2003) 1653–1658

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Epoxidation of styrene with iodosylbenzene in the presence of copper(II) Schiff-base complexes

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Received 14 September 2002; accepted 15 April 2003

Abstract

Copper(II) complexes with salen Schiff-base ligands derived from ethylenediamine or (*S*,*S*)-1,2-diphenylethylenediamine and salicylaldehyde or 5-methoxy, 5-bromo and 5-nitrosalicylaldehyde have been tested as catalysts for the epoxidation of styrene with iodosylbenzene, in dichoromethane as a solvent. The reactions were followed by gas chromatographic analysis and mass spectrometry. Catalytic activities were found to be dependent upon both the Lewis acidity of the metal complexes and the presence of phenyl substituents on the ethylene moiety. Moderate styrene conversions and epoxide yields were obtained. Pseudo-first-order kinetics was observed for the styrene conversion. Possible reaction mechanisms are outlined.

Keywords: Salen Cu(II) complexes; Schiff-base ligands; Catalytic epoxidation; Iodosylbenzene; Styrene; Hammett substituent constants

1. Introduction

Over the last decades the epoxidation of olefins catalyzed by metal complexes has become an important research area in both organic synthesis and bio-inorganic modeling of oxygen-transfer metalloenzymes [1–7]. Dissymmetric Schiff-base metal chelates are among the compounds most widely studied as catalysts for enantioselective epoxidation of prochiral unfunctionalized alkenes in organic solvents. Good overall epoxide yields and enantiomeric excess have been obtained with a variety of olefin substrates and oxygen atom sources by using chiral Schiff-base complexes of manganese(III) as catalysts [1,2,8,9]. In a somewhat lower status appears their analogues of manganese(II) [9], chromium(III) [10,11], ruthenium(III) [2] and ruthenium(II) [12]. Generally, it is accepted that the oxygen-transfer processes mediated by the above quoted complexes, and others such as iron(III), manganese(III) and chromium(III) porphirins [3], occur through pathways involving the formation of high-valent metal oxo intermediates. However, the fact that non-redox metal complexes can also behave as catalysts for alkene epoxidation by iodosylbenzene has lead to the proposal of alternative reaction mechanisms that involve the formation of metal–iodosylbenzene complexes as intermediates [6,7,13]. Similar pathways have been suggested for olefin epoxidation by iodosylbenzene in the presence of mono and binuclear copper(II) chelates of polydentate ligands with nitrogen-donors, or Cu^{2+} ion itself, as catalysts [4,5]. On the other hand, copper(II) complexes of *N*-glycosides have also been found to catalyze the epoxidation of alkenes by *tert*-butyl hydroperoxide or iodosylbenzene in acetonitrile or dichloromethane as solvents [14]. Even though Schiff-base copper(II) complexes have been known for nearly 100 years, no study about their catalytical properties in the epoxidation of olefins appears to have been reported to date. We have recently reported the synthesis, spectroscopic and electrochemical characterization of copper(II) complexes with Schiff-base ligands derived from ethylenediamine or dissymmetric 1,2-diphenylethylenediamines and salicylaldehyde or 5-methoxy, 5-bromo and 5-nitrosalicylaldehyde [15,16]. In the present work some of the above-mentioned copper(II) complexes, viz. the ethyle-

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doi:10.1016/S0277-5387(03)00326-7

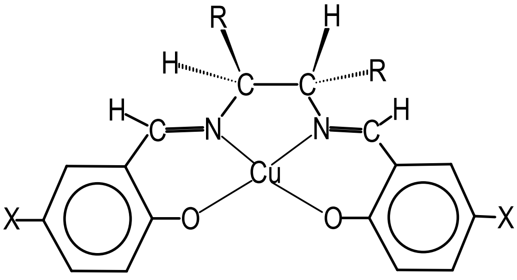
nediamine and (1*S*,2*S*)-1,2-diphenylethylenediamine derivatives, have been studied as potential catalysts for epoxidation of styrene by iodosylbenzene in dichloromethane as a solvent.

2. Experimental

Reagent grade chemicals and HPLC grade solvents were from Aldrich. Unless otherwise stated, they were used without further purification. Dichloromethane was dried and redistilled by current methods and stored under N_2 over molecular sieve before use. Styrene was passed through columns of activated neutral alumina in order to remove its stabilizing agent content. Iodosylbenzene was prepared by a procedure reported in the literature [17]. Copper(II) complexes were prepared as previously reported [15]. The sparing solubility of the complexes with nitro- and bromo-substituted Schiff-base ligands was a restrictive factor on selecting the concentration ranges for the epoxidation experiments. The procedure for the catalytic epoxidation of styrene was as follows: For each metal complex a stock solution in CH_2Cl_2 (10^{-4} M) was prepared. To 20 ml of copper(II) complex solution, 5 μl of GC internal standard (*n*-decane) and 2.5 μl of purified styrene were added. The resulting solution was diluted with CH_2Cl_2 to 50 ml in a volumetric flask at 30 °C. Before addition of the iodosylbenzene, an aliquot was taken, and the initial concentration of styrene was determined by GC/MS. Next, the solution was maintained at 30 °C, and the reaction was started by the addition of iodosylbenzene (4.4 mg, 20 μmol) and stirred at a constant speed under nitrogen atmosphere. For the sake of comparison, the reaction was also carried out in the absence of metal complex. Aliquots were taken at timed intervals and analyzed by GC/MS. All GC/MS analyses were performed on a Fison model MD 800 gas chromatograph coupled to a mass selective detector. UV–visible spectra were recorded on a UV3 Unicam spectrometer (220–750 nm).

3. Results and discussion

The copper(II) complexes under study were labeled as shown in Fig. 1. Results obtained for the reactions of styrene with iodosylbenzene in the presence of complexes **1S**–**4S** and **1**–**4** are presented in Figs. 2 and 3, respectively. Results for the reactions carried out in the absence of metal complexes were also included for comparison. In these figures, the time course of the reactions has been illustrated in terms of percentage of styrene conversion and epoxide yield. According to these data, in all of the reactions excepting the non-catalytic one, the conversion of styrene was considerably greater than the yield of epoxide. This fact could be ascribed to the occurrence of either side reactions during the epoxidation or further acid-catalyzed epoxide ring opening promoted by water, which is present in small amounts in the reaction media [6]. In the latter instance, the metal complexes themselves would be acting as acid catalysts. Accordingly, the time profiles for the epoxidation yields of some systems, viz. **1**–**4** and **2S**, suggest that there are two reactions occurring consecutively (Figs. 2 and 3). Taking into account the exceedingly small concentrations of metal complexes and styrene in the studied systems, it appears feasible that small water contents can exert some effects on the epoxidation yields, as the presence of water causes an increase in the amounts of allyllic oxidation products [6]. Indeed, in this study the initial concentrations of styrene and copper(II) complexes were approximately 4×10^{-4} and 4×10^{-5} M, respectively, i.e. of the same order as the water contents currently found in nonaqueous systems [18,19]. However, under the conditions employed for the GC analyses, only styrene, styrene oxide and iodobenzene were detected on the chromatograms.



1:	R = H,	X = OCH_3	1S:	R = C_6H_5,	X = OCH_3
2:	R = H,	X = H	2S:	R = C_6H_5,	X = H
3:	R = H,	X = Br	3S:	R = C_6H_5,	X = Br
4:	R = H,	X = NO_2	4S:	R = C_6H_5,	X = NO_2

Fig. 1. Structure and labeling of the copper(II) Schiff-base complexes.

For the studied systems only low to moderate styrene conversions and epoxide yields were obtained. Furthermore, complexes **1** and **1S** appear to behave rather as inhibitors since they gave rise to styrene conversion rates slower than that of the uncatalyzed reaction. Anyhow, complexes **2S**, **3S**, **4S** and **4** exhibited catalytic properties roughly similar to those of some binuclear complexes of manganese(II), cobalt(II), copper(II) and zinc(II) [5,6]. Moreover, both styrene conversion and epoxide yield data showed a clear dependence upon the electron withdrawing effects of the susbstituents on the phenolate moieties. Thus, for both series of copper(II) complexes the order $NO_2 > Br > H > OCH_3$ was observed (Figs. 2 and 3). It has previously been proposed that iodosylbenzene–metal complex adducts would be involved as intermediates in the reaction mechanism of the epoxidation of olefins by iodosylbenzene mediated by metal complexes [6,7,13]. In such adducts monomeric

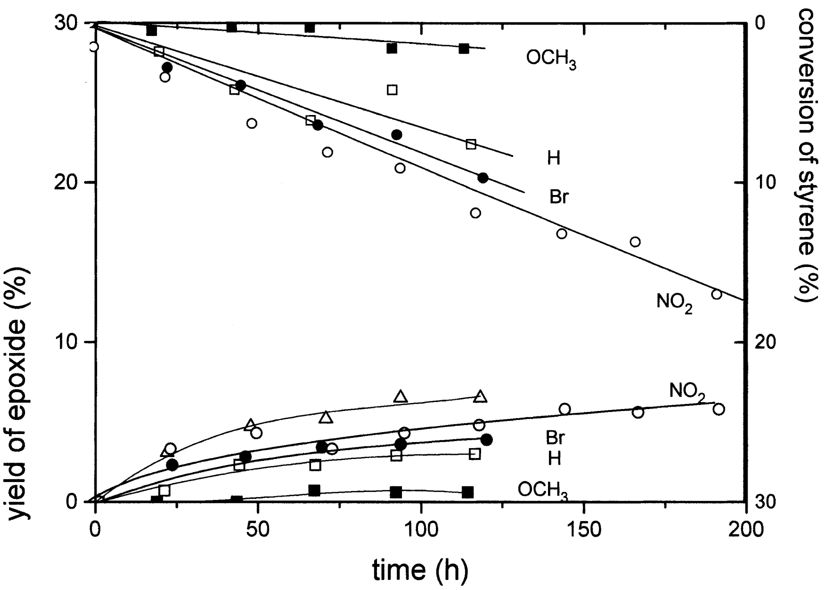


Fig. 2. Reaction profiles for the epoxidation of styrene with iodosylbenzene in the presence of complexes **1** (■); **2** (□); **3** (●); and **4** (○). No metal complex (△). The styrene conversion profile of the uncatalyzed reaction as been omitted for clarity.

iodosylbenzene would be coordinated to the metal center through the oxygen atom [13,20]. Hence, the above-mentioned sequence would be related to changes in the Lewis acidity of the axial coordination sites on the metal center over both series of copper complexes [21]. In addition to electronic effects, dependence of styrene conversions and epoxide yields upon steric effects also becomes apparent on comparing the time profiles of styrene conversion for the reactions mediated by each series of copper complexes, i.e. ethylenediamine and (1*S*,2*S*)-1,2-diphenylethylenediamine derivatives, with that of the noncatalytic reaction (Figs. 2 and 3). Accordingly, the styrene conversion mediated by complex **4S** occurs approximately five times faster than the noncatalytic one, whereas in the presence of complex **4** the reaction proceeds only 1.4 times faster. Similar but less conspicuous differences are observed between the styrene conversions mediated by complexes **3S** and **3**, which occur 3.2 and 1.3 times faster than the uncatalyzed reaction, respectively, and by complexes **2S** and **2**,

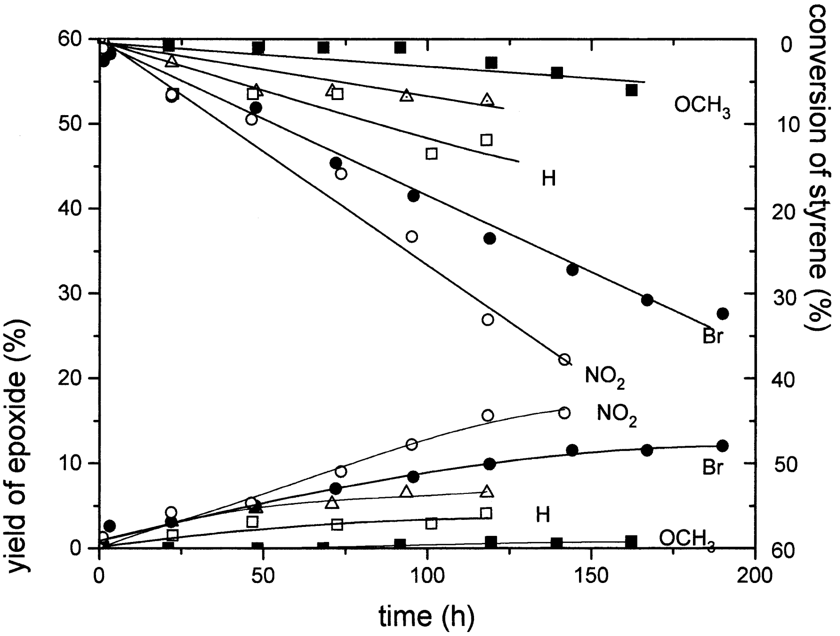


Fig. 3. Reaction profiles for the epoxidation of styrene with iodosylbenzene in the presence of complexes **1S** (■); **2S** (□); **3S** (●); and **4S** (○). No metal complex (△).

which occur 1.7 and 1.05 faster, respectively. By analogy to other catalytic systems [1,13,22], it was assumed that the steric effects arising from the phenyl substituents on the ethylenediamine moiety of the Schiff-base ligand contribute to an appropriate transition state orientation of the styrene molecule towards the iodine–oxygen bond of the iodosylbenzene monomer axially coordinated to the metal ion center. Though the occurrence of such steric effects suggests that some enantioselectivity should be expected for the epoxidation of styrene mediated by complexes **1S**–**4S**, determinations of enantiomeric excess were not carried out in the present study. On the other hand, in all cases the styrene conversion data were found to fit acceptably with both a pseudo-first-order and a zero-order kinetics in styrene. However, pseudo-first-order kinetics in styrene led to obtain somewhat better Hammett relationships and so was preferred. Pseudo-first-order plots for the reactions mediated by complexes **1S**–**4S** are shown in Fig. 4. Similar but more overlapped first-order plots resulted for the reactions mediated by complexes **1**–**4**. The resulting pseudo-first-order rate constants (k) are listed in Table 1. Moreover, the plotting of $\log(k/k_0) = \rho\sigma_p$ Hammett relationships, where the subscripts 0 and p refer to X = H and *para*-substitution, respectively, gives positive reaction constant values for both series of metal complexes, viz. $\rho \cong 0.9$ for **1S**–**4S** and $\rho \cong 0.7$ for **1**–**4**. These ρ values suggest the occurrence of an increase in electron density near the phenolate moieties in the transition state, which is in good agreement with the formation of intermediates $C_6H_5IO \cdot CuL$ and their further interaction with the olefin π-system. A Hammett plot of $\log(k/k_0)$ versus σ_p for the series **1S**–**4S** is shown in Fig. 5.

Spectrophotometric measurements in the UV–visible region of metal complex–iodosylbenzene mixtures, in CH_2Cl_2 as a solvent, showed that in conditions of excess iodosylbenzene (1:10) the characteristic spectral bands of complexes **1S** and **4S** undergo a decrease in absor-

Table 1
Pseudo-first-order rate constants (k) for the epoxidation of styrene with iodosylbenzene in the presence of the copper(II) Schiff-base complexes, in CH_2Cl_2, at 30 °C

Complex	K (h^{-1})	k/k_0 [a]	k/k'_u
1	$(1.7 \pm 0.9) \times 10^{-4}$	0.25	0.26
2	$(6.9 \pm 3.8) \times 10^{-4}$	1.00	1.05
3	$(8.4 \pm 1.5) \times 10^{-4}$	1.22	1.27
4	$(8.9 \pm 1.6) \times 10^{-4}$	1.29	1.35
1S	$(3.3 \pm 1.6) \times 10^{-4}$	0.30	0.50
2S	$(1.1 \pm 0.4) \times 10^{-3}$	1.00	1.67
3S	$(2.1 \pm 1.2) \times 10^{-3}$	1.91	3.18
4S	$(3.3 \pm 0.5) \times 10^{-3}$	3.00	5.00
No metal complex	$k'_u = (6.6 \pm 2.7) \times 10^{-4}$	–	1.00

[a] k_0 corresponds to k of the reaction in the presence of complex **2** or **2S** (X = H).

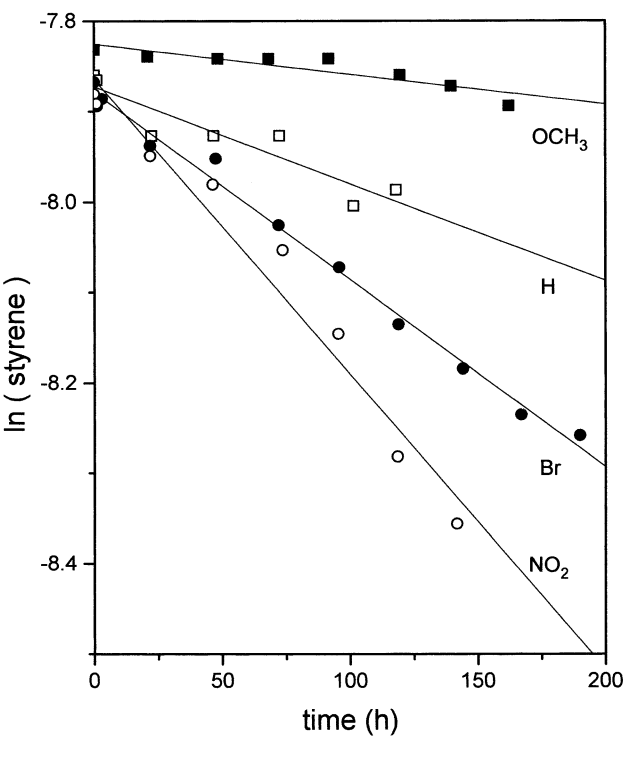


Fig. 4. Pseudo-first-order plots for the epoxidation of styrene with iodosylbenzene in the presence of complexes **1S** (■); **2S** (□); **3S** (●); and **4S** (○).

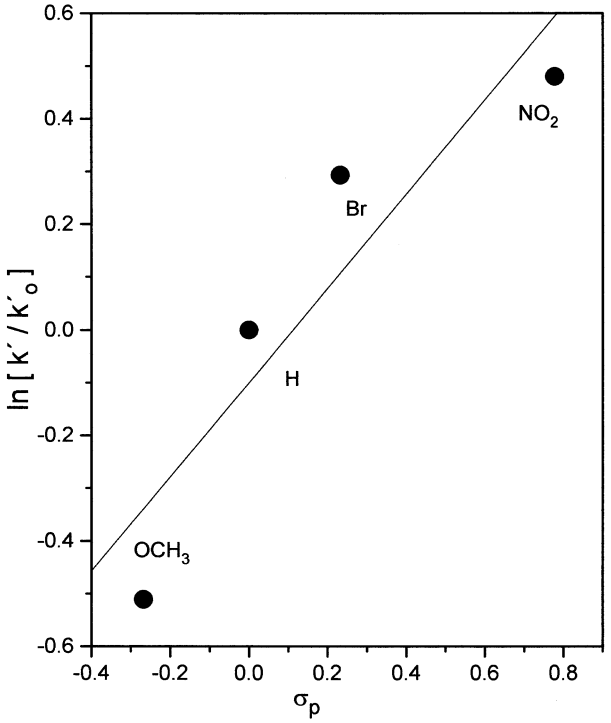


Fig. 5. Plot of $\log(k/k_0)$ versus the Hammett σ_p constants for the epoxidation of styrene with iodosylbenzene in the presence of copper(II) complexes with Schiff-base ligands derived from (1*S*,2*S*)-1,2-diphenylethylenediamine.

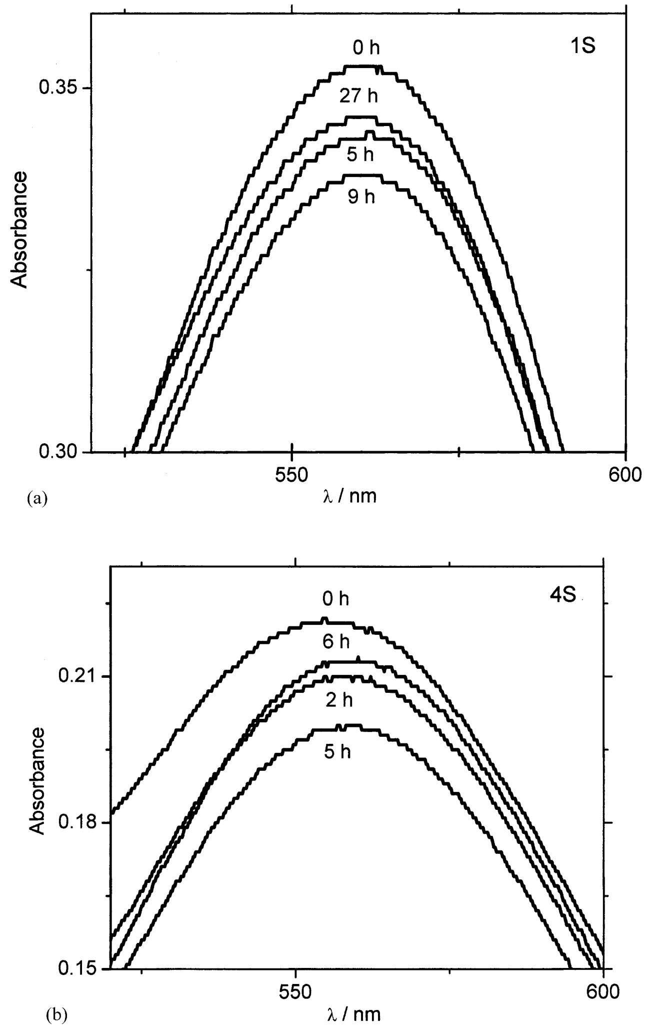


Fig. 6. Absorption spectra in the d–d band region of complexes **1S** and **4S** in CH_2Cl_2 at room temperature, before adding iodosylbenzene ($t = 0$); in the presence of 1:10 excess iodosylbenzene at some selected reaction times (hours).

bance, which is subsequently followed by an increase in absorbance (Fig. 6). This sequence of spectral changes would reflect a decrease in the concentration of the metal complexes, because of their adsorption on iodosylbenzene, followed by the formation of $CuL \cdot OIC_6H_5$ adducts. Moreover, differences in the observed rates of these spectral changes between **1S** and **4S** suggest that the tendency for formation of metal complex–iodosylbenzene adducts vary in the sequence $NO_2 > Br > H > OCH_3$, i.e. with the Lewis acidity of the axial coordination site on the metal complexes [21].

On the basis of the above considerations, and neglecting at present the possibility of simultaneous occurrence of the uncatalyzed reaction, the following reaction mechanism for the catalytic reactions was proposed:

$$C_6H_5IO(s) + CuL \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_6H_5IO \cdot CuL(s)$$

(metal complex adsorption)

$$C_6H_5IO \cdot CuL(s) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_6H_5IO \cdot CuL$$

(desorption of adduct)

$$C_6H_5IO \cdot CuL + C_6H_5CH{=}CH_2 \xrightarrow{k_3} \text{Products}$$

which leads to the rate equation:

$$-d[C_6H_5CH{=}CH_2]/dt = K_1K_2k_3[CuL]_o[C_6H_5CH{=}CH_2]/[1 + K_1(1 + K_2)] \quad (1)$$

where $K_2 = k_2/k_{-2}$, $K_1 = (k_1/k_{-1})(1 - \theta_c)c_s$ and $[CuL]_o$ is the total concentration of copper(II) complex. In the expression of K_1, θ_c is the fraction of adsorption sites which are covered by CuL, and c_s is the total concentration of surface sites per square centimeter. Thus, the pseudo-first-order constant would be:

$$k_c \approx K_1K_2k_3[CuL]_o/[1 + K_1(1 + K_2)] \quad (2)$$

and the rate equation becomes:

$$-d[C_6H_5CH{=}CH_2]/dt \approx k_c[C_6H_5CH{=}CH_2] \quad (3)$$

which is in good agreement with the reaction profiles experimentally observed for the styrene conversion. The pseudo-first-order kinetics in styrene necessarily involves $k_3 < k_2$, so the k data listed in Table 1 suggest that k_3 would be in the sequence $OCH_3 < H < Br < NO_2$, i.e. would increase with the Lewis acidity in both series of metal complexes. If the possibility of formation of $C_6H_5IO \cdot CuL$ intermediates is further considered, the k data would also reflect an increase in the electrophilic character of the iodine atom of the iodosylbenzene axially coordinated to the metal center over the above quoted sequence [6,7]. On the other hand, the comparison of the k values for both **1**–**4** and **1S**–**4S** series suggests that k_3 would increase with the steric effects arising from the phenyl substituents on the ethylenediamine moiety of the Schiff-base ligand.

For the uncatalyzed reaction the following mechanism is proposed:

$$C_6H_5IO(s) + C_6H_5CH{=}CH_2 \underset{k'_{-1}}{\overset{k'_1}{\rightleftarrows}} C_6H_5IO(s) \cdot C_6H_5CH{=}CH_2$$

(styrene adsorption)

$$C_6H_5IO(s) \cdot C_6H_5CH{=}CH_2 \xrightarrow{k'_2} \text{Products}$$

(reaction of styrene with OIPH(s) and desorption of products) from which:

$$-d[C_6H_5CH{=}CH_2]/dt \approx K'_1k'_2[C_6H_5CH{=}CH_2]/\{1 + K'_1[C_6H_5CH{=}CH_2]\} \quad (4)$$

where $K'_1 = k_1'/k'_{-1}$. Since styrene should be adsorbed in a weaker way than the copper(II) complexes, and

$[C_6H_5CH{=}CH_2] \ll 1$, the pseudo-first-order constant for the uncatalyzed reaction would correspond to: $k_u{}' \approx K'_1k'_2$, and the rate equation becomes:

$$-\mathrm{d}[C_6H_5CH{=}CH_2]/\mathrm{d}t \approx k'_u[C_6H_5CH{=}CH_2]. \tag{5}$$

If the occurrence of parallel catalyzed and uncatalyzed reactions in the systems under study is further considered, kinetic treatment should lead to a two term rate expression, in which both reactions contribute:

$$-\mathrm{d}[C_6H_5CH{=}CH_2]/\mathrm{d}t \approx (k_c + k_u)[C_6H_5CH{=}CH_2].$$

In this expression k_u is an effective pseudo-first-order rate constant for the uncatalyzed reaction, i.e. it includes the effects of the occurrence of a competitive adsorption between styrene and the metal complex. Explicitly, for the noncatalytic process the occurrence of a parallel catalyzed reaction implies that:

$$k'_1c_s(1 - \theta_u - \theta_c)[C_6H_5CH{=}CH_2] = k'_{-1}c_s\theta_u. \tag{6}$$

In this expression θ_u is the fraction of adsorption sites which are covered by styrene, and the other quantities have been previously defined. If $\theta_u \ll \theta_c$ is assumed, the preceding equation may be rearranged to

$$\begin{aligned}\theta_u &\approx (1 - \theta_c)(k'_1/k'_{-1})[C_6H_5CH{=}CH_2]\\ &= (1 - \theta_c)K'_1[C_6H_5CH{=}CH_2]\end{aligned} \tag{7}$$

and the effective pseudo-first-order constant for the parallel noncatalytic process results to be

$$k_u \approx (1 - \theta_c)K'_1k'_2 = (1 - \theta_c)k'_u. \tag{8}$$

Hence, a somewhat improved rate expression for the catalytic systems would be:

$$\begin{aligned}&-\mathrm{d}[C_6H_5CH{=}CH_2]/\mathrm{d}t\\ &\qquad \approx [k_c + (1 - \theta_c)k'_u][C_6H_5CH{=}CH_2]\end{aligned} \tag{9}$$

where $[k_c+(1-\theta_c)k'_u] \approx k$. This rate expression also accounts for the apparent inhibitory properties of complexes **1** and **1S** (see Figs. 2 and 3 and Table 1). Thus, from the data of Table 1 it can be inferred that for the reaction in the presence of such complexes $k_c < k'_u$. Moreover, Fig. 6 indicates that for these systems K_2 should be very small. Hence, θ_c should be large and the contribution of k'_u in the modified kinetic law should be rather low. In fact, taking $k_c > 0$ and $k < k'_u$, as is true for the systems **1** and **1S**, the inequalities $\theta_c > (1 - k/k'_u)$ and $k_c > \theta_c k'_u$ may, respectively, be derived. The former expression used for the system **1** yields the condition $\theta_c > 0.742$ as limiting value ($k_c = 0$); i.e. if $\theta_c = 0.742$ only the uncatalyzed reaction should occur, and the metal complex should exert a maximum inhibitory power. In turn, for the system **1S** the condition $\theta_c > 0.50$ is obtained. These results suggest that K_2 values are in the sequence **1S** > **1**. Probably, the occurrence of parallel reactions in the catalytic systems may be responsible for the rather moderate correlation coefficients obtained for the plots of $\log(k/k_0)$ versus the Hammett σ_p constants (Fig. 5).

Future studies in our laboratory, regarding the catalytic behaviour of Schiff-base copper(II) complexes on the epoxidation of olefins, will be directed towards the chemical modification of the ligands in order to increase the Lewis acidity of the axial coordination sites as well as to improve the solubility of their respective copper(II) complexes in aprotic solvents.

Acknowledgements

Financial support from FONDAP, project 11980002, is gratefully acknowledged.

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